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Electronic supplementary information (ESI) for

# One-pot Catalytic Selective Synthesis of 1,4-Butanediol from 1,4-Anhydroerythritol and Hydrogen

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## **Experimental details**

### Catalyst preparation

The ReO<sub>x</sub>/Support catalysts were prepared by impregnating support materials with NH<sub>4</sub>ReO<sub>4</sub> (Mitsuwa Chemicals Co. Ltd.) aqueous solution at 353 K. Support materials included carbon black "Black Pearl 2000 (BP2000)" (C-BP, Cabot Co., BET surface area: 1282 m<sup>2</sup>/g); extruded activated carbon "Norit RX3 extra" (C-NR, Cabot Co., BET surface area: 1159 m<sup>2</sup>/g); TiO<sub>2</sub> (Aerosil Co. Ltd., P25, BET surface area: 47 m<sup>2</sup>/g); SiO<sub>2</sub> (Fuji Silysia Co. Ltd., G-6, BET surface area: 535 m<sup>2</sup>/g); ZrO<sub>2</sub> (Daiichi Kigenso Kagaku Kogyo Co., Ltd., BET surface area: 62 m<sup>2</sup>/g),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Aerosil Co. Ltd., BET surface area: 82 m<sup>2</sup>/g), MgO (Ube Industries, Ltd., 500A, BET surface area: 34 m<sup>2</sup>/g). Supports except carbons were calcinated at 773 K for 3 h before impregnation. All the impregnated catalysts were dried in oven at 373 K for 12 h. Then the non-carbon-supported catalysts were calcinated 773 K for 3 h. The loading amount of Re was typically 3wt%.

The Au/CeO<sub>2</sub> catalyst was prepared by deposition–precipitation method.<sup>S1</sup> NaOH (Wako Pure Chemical Ind. Ltd.) aqueous solution (0.1 M) was added drop by drop to the stirring suspension of HAuCl<sub>4</sub>·4H<sub>2</sub>O (Wako Pure Chemical Ind. Ltd.) aqueous solution and CeO<sub>2</sub> (HS, Daiichi Kigenso Kagaku Kogyo Co., Ltd., calcinated at 873 K for 3 h, BET surface area: 84 m<sup>2</sup>/g) at 353 K until pH = 8. After 4 h stirring, the suspension of Au/CeO<sub>2</sub> was cooled to room temperature, then filtered and washed with 2 L distilled water. The Au/CeO<sub>2</sub> was dried at 373 K for 12 h, and then calcined at 673 K for 4 h. The Re was loaded on Au/CeO<sub>2</sub> by impregnation method using NH<sub>4</sub>ReO<sub>4</sub> (Mitsuwa Chemicals Co. Ltd.) aqueous solution for the preparation of ReO<sub>x</sub>-Au/CeO<sub>2</sub> catalyst. The ReO<sub>x</sub>-Au/CeO<sub>2</sub> was dried at 373 K for 12 h, and then calcinated at 373 K for 12 h, and then calcinated at 673 K for 4 h again. The loading amount of Re was 1%, and the Au/Re molar ratio was 0.3 (Au 0.3 wt%).

### Activity test

Activity tests were carried out in a 190 mL stainless steel autoclave. 1,4-Anhydroerythritol (1,4-AHERY, >98%; Tokyo Chemical Ind. Co., Ltd., substrate), dodecane (>99%; Tokyo Chemical Ind. Co., Ltd., internal standard), 1,4-dioxane (>99%, Wako Pure Chemical Ind., Ltd., solvent), appropriate amount of catalysts, and a spinner were put into an inner glass cylinder placed in the autoclave. The air in the autoclave after sealing was purged by flushing with H<sub>2</sub> (99.99%; Showa Denko K.K.) thrice. Then H<sub>2</sub>

pressure was increased to appropriate value. The stirring rate was 250 rpm (magnetic stirring). The autoclave was heated to the reaction temperature monitored via a thermocouple inserted in the autoclave. The reaction time started when the temperature reached the target temperature. The standard reaction conditions were: 0.5 g 1,4-anhydroerythritol, 0.15 g ReO<sub>x</sub>-Au/CeO<sub>2</sub>, 0.15 g ReO<sub>x</sub>/C-BP, 0.1 g dodecane (internal standard), 4 g 1,4-dioxane, 413 K reaction temperature, 8 MPa H<sub>2</sub> pressure (at reaction temperature), and 24 h reaction time. The parameters were changed appropriately for investigating the effects of reaction conditions. Details of the reaction conditions are described in each result. The tests of 2,5-dihydrofuran (2,5-DHF, >98%; Tokyo Chemical Ind. Co., Ltd.) and 2,3-dihydrofuran (2,3-DHF, >98%; Tokyo Chemical Ind. Co., Ltd.) were carried out in the similar method as above. The standard reaction conditions were: 0.15 g substrate, 0.04 g H<sub>2</sub>O (substrate: H<sub>2</sub>O = 1: 1), 0.15 g ReO<sub>x</sub>-Au/CeO<sub>2</sub> or ReO<sub>x</sub>/C-BP, 0.1 g dodecane, 4 g 1,4-dioxane, 413 K reaction temperature, 8 MPa hydrogen pressure (at reaction temperature), and 4 h reaction time.

After reaction of all tests, the reactor was cooled down. The gases were collected in a gas bag. The liquid and catalysts in autoclave were transferred to vials, and the catalysts were separated by centrifugation. The products were analyzed by FID-GC (Shimadzu GC-2025) with TC-WAX capillary column (diameter 0.25 mm, 30 m), GC–MS (QP5050, Shimadzu), and nuclear magnetic resonance (NMR, Fourier 300HD, Bruker Co.).

At first, the carbon balance (C.B.) of each analysis result was calculated using eqn (1). Here, the unidentified products were detected in the GC analysis, the sum of these products are denoted as "others" in each result. The amount of "others" was calculated on the assumption that the sensitivity of "others" are the same as that of 1,4-butanediol (1,4-BuD) unless denoted.

When the C.B. is in the range of  $100 \pm 10\%$  considering the experimental error, the conversion and selectivity on the carbon basis are calculated by eqn (2) and (3), respectively. The data of C.B. are not shown in each result. In contrast, when the C.B. is clearly lower than 100% (<90%), the conversion and selectivity on carbon basis are calculated by eqn (4) and (5) as below. The selectivity of "others" is the same as the above case. The data of C.B. clearly below 100% are shown in each result. We think two reasons for low C.B. in the results. One is a substrate with low boiling point, in particular, 2,3-DHF. (b.p. 328 K). In the experiments of 2,3-DHF substrate (Table 3, entries 8-11), and in the results of significant

yield of 2,3-DHF product in the reaction of 1,4-anhydroerythritol (Table 1, entries 3-5), it is thought that a part of 2,3-DHF can be lost during the purge of  $H_2$  before reaction and the filtration after reaction. The other reason is the side reactions such as polymerization of unsaturated compounds like 2,5-DHF or 2,3-DHF giving undetected products, and this phenomenon seems to be observed remarkably on ReO<sub>x</sub>/C-BP in Table 3, entries 1 and 4. The yield was calculated by eqn (6).

C. B. (%)=
$$\frac{\text{Amount of remaining substrate (C-mol) + Total amount of detected products (C-mol)}{\text{Amount of initial substrate (C-mol)}} \times 100$$
(1)

$$Conversion (\%) = \frac{Total amount of detected products (C-mol)}{Amount of remaining substrate (C-mol) + Total amount of detected products (C-mol)} \times 100$$
(2)

Selectivity of product A (%)=
$$\frac{\text{Amount of A (C-mol)}}{\text{Total amount of detected products (C-mol)}} \times 100$$
(3)

$$Conversion (\%) = 100 - \frac{Amount of remaining substrate (C-mol)}{Amount of initial substrate (C-mol)} \times 100$$
(4)

Selectivity of product A (%)= $\frac{\text{Amount of A (C-mol)}}{\text{Amount of initial substrate (C-mol) - Amount of remaining substrate (C-mol)}} \times 100$  (5)

$$\text{Yield (\%)} = \frac{\text{Conversion (\%)} \times \text{Selectivity (\%)}}{100} \tag{6}$$

The reuse procedure of catalysts was as follows: after reaction, the mixture of ReO<sub>x</sub>-Au/CeO<sub>2</sub> and ReO<sub>x</sub>/C-BP was washed by 1,4-dioxane, and centrifuged to remove the liquid, and then dried at 373 K for 12 h. The dried catalyst was treated with various conditions for regeneration. The tested regeneration methods included heating in air at 573 K for 4 h, heating in H<sub>2</sub> at 773 K for 3 h, and heating in N<sub>2</sub> at 773 K for appropriate hours. Due to the weight loss (40%, in four times use) during the recovery process, the weight of substrate and solvent in the next run was adjusted according to the amount of recovered catalyst mixture. The leached Re amount from the catalysts into the reaction solution was analyzed by inductively-coupled plasma atomic emission spectrometry (ICP-AES, ThermoFisher iCAP6500). The catalyst was removed from the liquid phase in glove bag or in air after cooling. The leached amount of Re is represented by its ratio to the total Re amount in Re catalysts.

#### Catalyst characterization

The samples of  $\text{ReO}_x$ -Au/CeO<sub>2</sub> and  $\text{ReO}_x$ /C-BP were characterized by X-ray diffraction (XRD), temperature-programmed reduction (H<sub>2</sub>-TPR), and thermogravimetric-differential thermal analysis (TG-DTA). XRD patterns were recorded by a diffractometer (Rigaku MiniFlex600). Cu K $\alpha$  radiation was used as an X-ray source. In the H<sub>2</sub>-TPR, 50 mg catalyst in a fixed-bed reactor equipped with a thermal conductivity detector (TCD) was reduced by 5% H<sub>2</sub> diluted with Ar (30 ml/min) from room temperature to 1173 K at a heating rate of 10 K/min. TG-DTA was carried out with Rigaku Thermo plus EVOII under air. Scanning transmission electron microscope (STEM) images were taken by JEOL ARM-200F with Cu grids.

### Products determination

Most products were determined by commercially available chemicals include tetrahydrofuran (THF, >98%, Wako Pure Chemical Ind. Ltd.), 2,5-DHF, 2,3-DHF, γ-butyrolactone (GBL, >99%, Wako Pure Chemical Ind. Ltd.), 1-butanol (1-BuOH, >99.7%, Wako Pure Chemical Ind. Ltd.), furan (>98%, Wako Pure Chemical Ind. Ltd.), 3-hydroxytetrahydrofuran (3-HTHF, >95%, Wako Pure Chemical Ind. Ltd.). The acetals which are commercially unavailable were isolated by column chromatography (silica gel; diethyl ether and ethyl acetate mixture) and was qualitatively analyzed by GC-MS and NMR. They include:



3,4-(4-hydroxybutylidenedioxy)-tetrahydrofuran (about 1:1 mixture

of stereoisomers), MW = 174.





NMR of about 1:1 mixture of stereoisomers:

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.153-1.295 (2H, m), 1.551-1.677 (6H, m), 1.700-1.765 (2H, m), 3.323-3.373 (2H, q), 3.416-3.466 (2H, q), 3.538-3.604 (4H, m), 3.974-4.038 (4H, d), 4.577-4.524 (2H, q), 4.664-4.710 (2H, q), 4.840-4.877 (1H, t), 5.101-5.137 (1H, t) ppm.

<sup>13</sup>C NMR (CDCl<sub>3</sub>): 25.6, 25.7, 28.5, 29.1, 61.3, 61.3, 72.1, 73.4, 79.1, 80.0, 104.7, 105.0 ppm.



This spectrum agrees with the literature (NIST #151913).

(S1) S. Tazawa, N. Ota, M. Tamura, Y. Nakagawa, K. Okumura and K. Tomishige, ACS Catal. 2016, 6, 6393-6397.



**Fig. S1** XRD patterns of ReO<sub>x</sub>-Au/CeO<sub>2</sub> (Re = 1 wt%, Au = 0.3 wt%) and ReO<sub>x</sub>/C-BP (Re = 3 wt%) catalysts. (a) CeO<sub>2</sub>, (b) ReO<sub>x</sub>-Au/CeO<sub>2</sub>, (c) ReO<sub>x</sub>-Au/CeO<sub>2</sub> + ReO<sub>x</sub>/C-BP, (d) ReO<sub>x</sub>-Au/CeO<sub>2</sub> + ReO<sub>x</sub>/C-BP after reaction (1,4-AHERY = 0.5 g,  $W_{\text{cat ReO}_x\text{-Au/CeO}_2$  = 0.15 g,  $W_{\text{cat ReO}_x\text{-CBP}}$  = 0.15 g, 1,4-Dioxane = 4 g,  $P_{\text{H}_2}$  = 8 MPa, T = 413 K, t = 24 h).



**Fig. S2** TG-DTA graph of the 1:1 mixture of  $\text{ReO}_x$ -Au/CeO<sub>2</sub> (Re = 1 wt%, Au = 0.3 wt%) and  $\text{ReO}_x$ /C-BP (Re = 3 wt%) (after 1st use). Heating rate = 10 K/min, sample weight = 10 mg.

Entry	Time /h	Conv. /%	Product selectivity /%								
			1,4-BuD	THF	2,5-DHF	2,3-DHF	GBL	1-BuOH	Acetal	Others	
1	1	33	28	3	3	0	2	1	55	10	
2	2	41	37	3	3	0	2	1	45	9	
3	4	49	55	4	1	0	2	2	28	7	
4	12	79	81	6	0	0	2	2	4	4	
5	16	89	84	6	0	0	2	2	2	3	
6	24	100	86	8	0	0	2	2	0	3	
7	48	100	82	13	0	0	0	2	0	2	
8	96	100	71	24	0	0	0	2	0	3	

Table S1 Time course of the reaction of 1,4-AHERY over the mixture of ReO<sub>x</sub>-Au/CeO<sub>2</sub> + ReO<sub>x</sub>/C-BP<sup>a</sup>

<sup>*a*</sup> 1,4-AHERY = 0.5 g,  $W_{\text{cat}(\text{ReO}_x\text{-Au/CeO}_2, \text{Re}=1 \text{ wt\%}, \text{Au}=0.3 \text{ wt\%})} = 0.15 \text{ g}, W_{\text{cat}(\text{ReO}_x\text{/C-BP}, \text{Re}=3 \text{ wt\%})} = 0.15 \text{ g}, 1,4\text{-Dioxane} = 4 \text{ g}, P_{\text{H}_2} = 8 \text{ wt\%}$ 

MPa, T = 413 K, t = 1 to 96 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, GBL:

*y*-butyrolactone, BuOH: butanol, Acetal: 3,4-(4-hydroxybutylidenedioxy)-tetrahydrofuran.

Table S2 Effect of solvent in the reaction of 1,4-AHERY over ReO<sub>x</sub>-Au/CeO<sub>2</sub> + ReO<sub>x</sub>/C-BP<sup>*a*</sup>

Entry	Solvent	Conv. /%	Product selectivity /%							
			1,4-BuD	THF	2,5-DHF	2,3-DHF	GBL	1-BuOH	Acetal	Others
1	None	88	88	2	0	0	0	3	4	3
2	1,4-Dioxane	100	86	8	0	0	2	2	0	3
3	THF	79	89	—	0	0	2	3	2	5
4	Water	8	42	1	0	0	0	1	0	55

<sup>*a*</sup> 1,4-AHERY = 0.5 g,  $W_{\text{cat}(\text{ReO}_x-\text{Au/CeO}_2, \text{Re}=1 \text{ wt\%}, \text{Au}=0.3 \text{ wt\%})} = 0.15 \text{ g}, W_{\text{cat}(\text{ReO}_x/\text{C-BP}, \text{Re}=3 \text{ wt\%})} = 0.15 \text{ g}, \text{ solvent} = 0 \text{ or } 4 \text{ g}, P_{\text{H}_2} = 8 \text{ solven} = 0.15 \text{ g}, W_{\text{cat}(\text{ReO}_x-\text{Au/CeO}_2, \text{Re}=1 \text{ wt\%})} = 0.15 \text{ g}, W_{\text{cat}(\text$ 

MPa, T = 413 K, t = 24 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, GBL:  $\gamma$ -

butyrolactone, BuOH: butanol, Acetal: 3,4-(4-hydroxybutylidenedioxy)-tetrahydrofuran.